Antifouling Paint Pollution in CA

PREC 2011

Nan Singhasemanon

DPR – Environmental Monitoring Branch

1

AFP Use & Pollution in CA

- "Blame it on Tributyl Tin"
- Sudden shift to copper AFPs
- Shelter Island Yacht Basin (SIYB) – San Diego
  - copper TMDL (late 1990's)
  - passive leaching & in-water hull cleaning
- MdR & Lower Newport Bay Metals TMDLs
- DPR initiated broader investigations
- Copper AFP Sub-Workgroup (2004 & ongoing)
  - gather existing data & identify gaps
  - coordinate CA studies
- DPR Multi-Regional Study (Summer/Fall 2006) – basis for Cu AFP Reevaluation

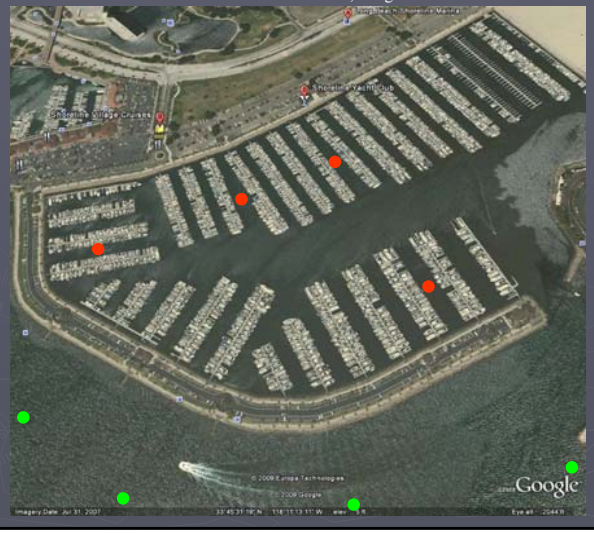
2

DPR Study Objectives

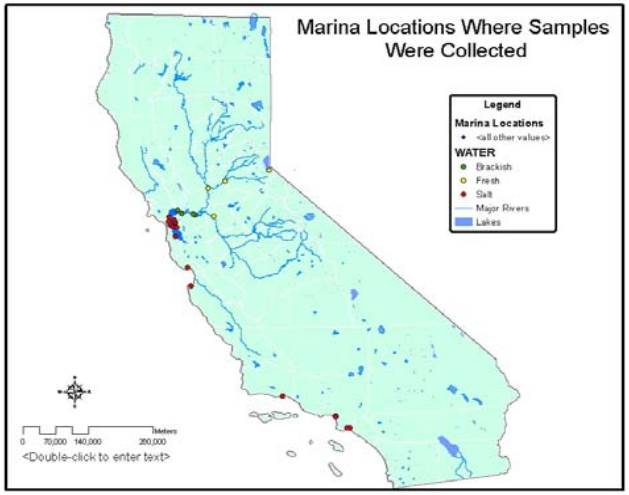
1. Assess the occurrences of AFP biocide indicators (i.e., Cu, Zn, and Irgarol/M1) & the magnitude of their concentrations in various marina areas of CA
2. Determine whether concentrations exceed water quality standards, criteria, guidelines or other relevant benchmarks?
3. Marina vs. Background?
4. Fresh vs. Brackish vs. Salt water marinas?
5. Measure toxicity of marina waters & confirm identity of toxicant
6. Apply predictive toxicity models to ascertain potential copper toxicity on a larger scale

3

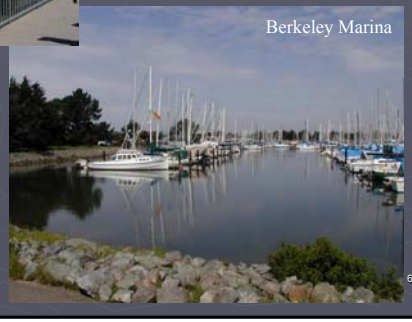
Downtown Shoreline Marina, Long Beach



4



Results



6

DCu Results

- Generally… salt > brackish > fresh
- High in Central & South Coast marinas (except 1 location)
  - within range of DCu results from 2 other studies in SoCal
- Low to Moderate in SF Bay Area, brackish & riverine marinas
- Low (< 1 ppb) in the 2 lake marinas
- MdR Basins consistently very high in DCu
  - higher than SIYB

7

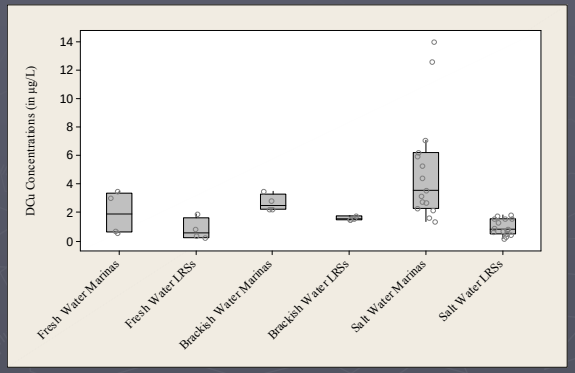
Median Dissolved Cu Concentrations - DPR 2006 Study

Marina	Marina Median in ug/L (ppb)	LRS Median in ug/L (ppb)	Estimated Number of Slips
Folsom Lake Marina	0.5	0.3	675
Tahoe Keys Marina	0.6	0.2	250
San Francisco Marina	1.1	0.4	700
Alamitos Bay Marina	1.2	0.3	1,191
Coyote Point Marina	2.1	1.3	565
Antioch Marina	2.2	1.5	310
Pittsburg Marina	2.1	1.5	486
South Beach Harbor	2.2	0.7	700
Clipper Yacht Harbor	2.4	0.8	735
Marina Bay Yacht Harbor	2.6	1.7	850
Benicia Marina	2.7	1.7	320
Sacramento Marina	3.0	0.7	547
Ballena Isle Marina	2.8	1.4	504
Village West Marina	3.4	1.8	700
Vallejo Marina	3.4	1.5	800
Berkeley Marina	3.3	0.7	1,052
Santa Cruz Harbor	4.3	0.3	1,000
Monterey Harbor	4.9	0.2	413
Santa Barbara Harbor	5.7	0.1	1,133
Loch Lomond Marina	5.8	1.7	517
Downtown Shoreline Marina	6.6	0.7	1,800
Marina del Rey Front Basins	12.4	1.0	~4500
Marina del Rey Back Basins	13.6	1.0	~2500

fresh water
brackish water
salt water

8

Marina Median DCu Concentrations by Water Types



9

Results - DCu (cont.)

- DCu in marina ↑ vs. DCu in LRS for marinas of all 3 water types *(statistically significant → marina source & lower flushing?)*
- DCu in salt & brackish water marinas ↑ vs. DCu in fresh water marinas *(statistically significant → higher use?)*
- All these numbers, but what is the context ???
- Many salt & brackish marinas exceeded W.Q. standards of the CA Toxics Rule or CTR (est. 2000)
  - 16 of 17 marinas exceeded CTR chronic stds. (3.1 ppb)
  - 10 of these 16 marinas also exceeded acute stds. (4.8 ppb)
- LRS samples rarely exceeded stds.

10

Results - DCu (cont.)

- **30%** of samples from salt & brackish water samples exceeded chronic stds.
- **17%** of these also exceeded acute stds.
- For fresh water, **none** of the samples exceeded fresh water CTR stds.

- *CTR violation = "likely to present a significant risk to aquatic organisms & their uses"* → 303d list → TMDLs

11

Results - Toxicity/TIE

- Endpoint → abnormal mussel embryo development & mortality
- 8 of 47 samples (17%) were toxic
  - 7 of 8 toxic samples came from MdR
- TIE → Cu is cause of toxicity

- *Toxicity is a violation of Water Boards narrative standards* → 303d list → TMDLs

12

Results - Predicted Toxicity Models

- Models → "will this sample be toxic?"
- Can be done for all samples, is site specific, & accounts for bioavailability
- In fresh water, BLM (fish gill effects) predicted virtually no Cu toxicity
- In salt water, BLM predicted Cu toxicity to mussel embryo in 18% of all samples
- 98% of samples w/ predicted Cu toxicity were marina samples

13

In Summary…

- Marinas are localized sources of Cu…(also Zn & Irgarol/M1)
- Boat AFPs are a significant source of Cu in salt & brackish water marinas during dry periods
- Ecological impacts from DCu are unlikely in fresh water marinas
- However, high DCu could adversely impact sensitive marine species
- Cu Toxicity at MdR - plus salt water BLM predicts more widespread Cu toxicity
- Other CA studies support our findings
- More details in DPR report
- A number of mitigation activities/projects are occurring, but outside the scope of this presentation

14

CCR 6220 (Authority – Reevaluation)

- "The director may, at any time, evaluate a registered pesticide… The director shall investigate all reported episodes and information… that indicate a pesticide may have caused, or is likely to cause, a significant adverse impact…. If the director finds from the investigation that a significant adverse impact has occurred or is likely to occur…, the pesticide involved shall be reevaluated."

15

Thank you.

Nan Singhasemanon
Staff Environmental Scientist/MAA Coordinator
Environmental Monitoring Branch
Surface Water Protection Program
1001 I St., Sacramento, CA 95812
nsinghasemanon@cdpr.ca.gov
(916) 324-4122

16

Update of DPR's Copper Based Antifouling Paint Reevaluation

Richard Spas
Reevaluation Coordinator
January 21, 2011

17

List of Registrants

- Blue Water Marine Paint
- Flexabar Corporation
- Flexdel Corporation
- Hempel Coatings (USA) Inc.
- International Paint, LLC
- Jotoun Paints, Inc.
- Kop-Coat, Inc.
- Marine Development & Research Corp.
- New Nautical Coatings, Inc.
- Rust-Oleum Corporation
- Sigmakalon USA LLC
- THE Sherwin-Williams Co.

18

Reevaluation Timeframes

- 0 days — Initiation of the reevaluation.
- 90 days — Compliance proposal.
- 120 days — Submission of existing leach rate data.
- 180 days — Submission of a mitigation strategy.

19

Compliance Proposal and Identification

90 days

- Intent to comply with the leach rate data requirements, mitigation strategies, and follow-up water monitoring.
- The registrant's knowledge and identification of existing data.
- Categorization of the registered paint types into one of the six categories.
- Feedback and questions they might have.

20

Categorization of Paint Types

Paint Type Qualifier	Paint Type	Antifouling Method	Environmental Considerations	Durability
A	Soft Sloughing	Free leaching & soft. Paint erodes until completely disintegrated. 20-50% copper	Potential to release much toxicant due to uncontrolled sloughing	1 year or less
B	Epoxy Ester, Conventional	Hard, smooth finish. Releases toxicant by leaching. Up to 76% copper	Initial high release of toxicant, replaced by even copper leaching	approx. 2 years
C	Vinyl, Conventional	Hard, smooth finish. Releases toxicant by leaching. 40-67% copper	Better controlled release rate of copper vs. epoxy ester paint	approx. 2 years
D	Vinyl, Thin Film Teflon	Hard, smooth finish. Releases copper by leaching. 42% copper	Controlled leach rate of copper. Very hard finish	1-1.5 years
E	Copolymer, Ablative	Continuously sheds outer layer to release toxicant 46-58% copper	Boat use & underwater cleaning release toxicant	2 years Does not oxidize in air
F	Water-based, Ablative	Continuously sheds outer layer to release toxicant Up to 64% copper	Boat use & underwater cleaning release toxicant	approx. 2 years

21

Responses Received

Paint Type Category	# of Pesticide Products*
Copolymer, Ablative	23
Epoxy Ester, Conventional	36
Vinyl, Conventional	7
Water-based, Ablative	6

*Only 38% of the products are represented.

22

Submission of Existing Leach Rate Data

120 days

- Provide existing leach rate data already generated using either ASTM method:

1. American Society for Testing Method (ASTM) - Organotin Release Rates of Antifouling Coating Systems in Sea Water (ASTM D5108-90);
2. ASTM Test Method - Standard Test Method for Determination of Copper Release Rate from Antifouling Coatings in Substitute Ocean Water (ASTM D6442-06).

23

ASTM vs. ISO?

- Late 2010, International Standards Organization (ISO) was made available.

  ISO 10890:2010 – "Paints and Varnishes – Modeling of biocides release rate from antifouling paints by mass balance calculation."
- DPR is investigating alternate leach rate methodology.
- DPR considering possible extension of time.

24

Submission of Mitigation Proposal

- Identify and submit specific mitigation strategies to reduce dissolved copper concentrations below California Toxic Rule (CTR) or regionally applicable standards.
- Received some mitigation strategies for consideration.

25

Questions?

Richard Spas
Antifouling Paint Reevaluation Coordinator
916.322.9522
rspas@cdpr.ca.gov

26